BNL-91297-2010-CP

KINETICS OF SMALL PARTICLE ACTIVATION IN SUPERSATURATED VAPORS

McGraw, R. and Wang, J.

April 2010

For presentation at the
International Aerosol Conference 2010
Helsinki, Finland
Aug. 29-Sept. 3, 2010

Environmental Sciences Department/Atmospheric Sciences Division

Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This work was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Kinetics of small particle activation in supersaturated vapors

McGraw, Robert and Wang, Jian

Environmental Sciences Department, Brookhaven National Laboratory, 11973, New York, USA

Keywords: nucleation kinetics, wetting, heterogeneous condensation, barrier crossing.

We examine the nucleated (with barrier) activation of perfectly wetting (zero contact angle) particles ranging from bulk size down to one nanometer. Thermodynamic properties of the particles, coated with liquid layers of varying thickness and surrounded by vapor, are analyzed. Nano-size particles are predicted to activate at relative humidity below the Kelvin curve on crossing a nucleation barrier, located at a critical liquid layer thickness such that the total particle size (core + liquid layer) equals the Kelvin radius (Fig. 1). This barrier vanishes precisely as the critical layer thickness approaches the thin layer limit and the Kelvin radius equals the radius of the particle itself.

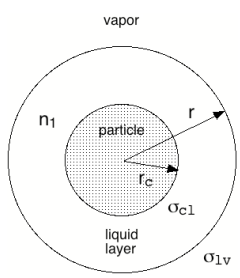

Figure 1. Schematic illustration of a spherical particle of radius r_c coated with n_1 molecules of liquid layer.

These considerations are similar to those included in Fletcher's theory (Fletcher, 1958) however the present analysis differs in several important respects. Firstly, where Fletcher used the classical prefactor-exponent form for the nucleation rate, requiring separate estimation of the kinetic prefactor, we solve a diffusion-drift equation that is equivalent to including the full Becker-Döring (BD) multi-state kinetics of condensation/evaporation along the growth coordinate. We also determine the mean first passage time (MFPT) for barrier crossing (Wedekind et al., 2007), which is shown to provide a generalization of BD nucleation kinetics especially useful for barrier heights that are considerably lower than those typically encountered in homogeneous vapor-liquid nucleation, and make explicit comparisons between the MFPT and BD kinetic models.

Barrier heights for heterogeneous nucleation are computed by a thermo-dynamic area construction introduced recently to model deliquescence and efflorescence of small particles (McGraw and Lewis, 2009). In addition to providing a graphical representation of the activation process that offers new insights, the area construction provides a molecular approach that avoids explicit use of the interfacial tension. Typical barrier profiles for water condensation on particles of different size are shown in Fig. 2. The main emphasis of this paper lies in the computation of these barriers and barrier crossing rates by the various methods described.

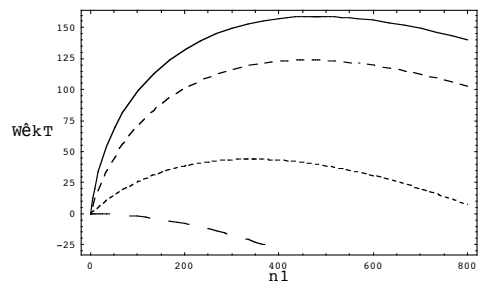

Figure 2. Reversible work required to coat particles of different sizes with n_1 molecules of liquid water from the vapor phase having a saturation ratio S=2.0. Curves top to bottom: no seed (homogeneous nucleation), 5Å (radius) seed, 10Å, and 15Å, which is equal to the Kelvin radius at this saturation ratio resulting in the absence of barrier for this size.

The present theory is especially relevant to determining the lower size limit for particle detection in condensation particle counters. Recently it has been shown that particles can take on liquid at sizes significantly smaller than predicted from the Kelvin relation in the no-barrier case (Winkler et al., 2008). This implies a detection principle based on the activated nucleation model that is the focus of the present study. Calculations are presented for water, n-propanol, and several other condensable vapors.

This work was supported by the DOE Atmospheric Science Program (now Atmospheric System Research)

Fletcher, N. H. (1958), *J. Chem. Phys*. 29, 572-576/

McGraw, R. & Lewis, E. R. (2009), *J. Chem. Phys.* 131, 194705 (1-14).

Wedekind, J., Strey, R. & Reguera, D. (2007), *J. Chem. Phys.* 126, 134103 (1-7).

Winkler, P. M. et al. (2008). *Science,* 319, 1374-1377.